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Natalie Kehrwald, Roberta Zangrando, Paolo Gabrielli, Jean-Luc Jaffrezo, Claude Boutron, Carlo Barbante, Andrea Gambaro

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Levoglucosan as a specific marker of fire events in Greenland snow

By NATALIE KEHRWALD[1]*, ROBERTA ZANGRANDO[2], PAOLO GABRIELLI[3,4], JEAN-LUC JAFFREZO[5], CLAUDE BOUTRON[5,6], CARLO BARBANTE[1,2,7] and ANDREA GAMBARO[1,2], [1]*Department of Environmental Sciences, Informatics and Statistics, University of Venice, Ca' Foscari 30123, Venice, Italy;* [2]*Institute for the Dynamics of Environmental Processes-National Research Council, 30123, Venice, Italy;* [3]*School of Earth Sciences, The Ohio State University, Columbus, Ohio 43210, USA;* [4]*Byrd Polar Research Center, The Ohio State University, Columbus, Ohio 43210, USA;* [5]*Laboratoire de Glaciologie et Géophysique de l' Environnement (UMR Université Joseph Fourier/CNRS 5183), 54 rue Molière, BP 96, 38402, Saint Martin d' Hères cedex, France;* [6]*Unité de Formation et de Recherche "Physique, Ingénierie, Terre, Environnement, Mécanique", Université Joseph Fourier de Grenoble (Institut Universitaire de France), 715 rue de la Houille Blanche, BP 53, 38041, Grenoble cedex, France;* [7]*Accademia Nazionale dei Lincei, "Centro Beniamino Segre", via della Lungara 10 00165, Rome, Italy*

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ABSTRACT

We demonstrate the use of levoglucosan (1,6-anhydro-β-D-glucopyranose) as a source-specific proxy of past fire activity in snow pits and ice cores. Levoglucosan is unambiguously a degradation product derived from cellulose burning at temperatures greater than 300 °C and is widely used as a biomass burning marker in aerosol analyses. We analyse samples collected from a 3 m snow pit at Summit, Greenland (72°20′N, 38°45′W; 3270 m a.s.l.), with a known depositional history where biomass burning aerosols were traced from their source in a Canadian smoke plume, through their eastward transport and deposition on the Greenland ice sheet, and their eventual burial by accumulating snow layers. The snow pit levoglucosan profile replicates oxalate concentrations from a known forest fire event, suggesting the applicability of levoglucosan as a marker of past fire activity in snow and by extension in ice cores. However, levoglucosan concentration peaks in the snow pit differ from those of ammonium and potassium, which are traditionally used as biomass burning proxies in snow and ice studies but which incorporate sources other than fire activity. The source specificity of levoglucosan can help determine the past relative contribution of biomass burning aerosols when used in conjunction with other proxies in snow and ice.

Keywords: biomass burning, levoglucosan, snow, ice core, Greenland

1. Introduction

Biomass burning aerosols are one of the least understood aspects of the modern climate system and even less is known about their past influence (Solomon et al., 2007). Ice cores and snow pits provide essential information regarding past atmospheric chemistry, and proxies such as ammonium, potassium, oxalate and isotopic ratios in methane (CH_4) or carbon monoxide (CO) have been used to estimate previous periods of increased fire activity (Echalar et al., 1995; Legrand and DeAngelis, 1996; Stohl et al., 2007; Fischer et al., 2008; Wang et al., 2010). Fires influence climate and regional ecology by changing primary productivity, biodiversity (Power et al., 2008) and releasing atmospheric aerosols that provide cloud condensation nuclei (Jimenez et al., 2009). Organic aerosols comprise up to 90% of the submicron particulate mass in biomass burning emissions (Zhang et al., 2007). Biomass burning including landscape fires emits 2–4 versus 7.2 Pg C yr^{-1} emitted by fossil-fuel burning and therefore produces up to 50% as much carbon dioxide as fossil-fuel combustion (Andreae and Merlet, 2001; Van der Werf et al., 2006; Solomon et al., 2007; Bowman et al., 2009) and caused up to 65% of the variability in the carbon dioxide growth rate between 1997 and 2001

*Corresponding author.
email: kehrwald@unive.it

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(Bowman et al., 2009). Biomass burning aerosols have a major anthropogenic component with a significant direct radiative forcing (Solomon et al., 2007) and therefore may influence future climate change.

Ice cores and snow pit samples contain specific molecular markers and other pyrochemical evidence which provide much-needed information on the role of fire in driving past climate and the possibility of current biomass burning affecting future global climate. Ice and snow studies have extensively documented large changes in aerosol constituents including ionic species (Udisti et al., 2004; Edwards et al., 2006), dust (Basile et al., 1997; Biscaye et al., 1997; Ruth et al., 2008), trace elements (Gabrielli et al., 2005; Fortner et al., 2009) and organic compounds (Grannas et al., 2006) during the late Quaternary period. Many studies focus on establishing episodic biomass burning events as recorded in snow and ice using elevated concentrations of various chemical species, including black carbon and soot (Hansen and Nazarenko, 2004), ammonium (Stohl et al., 2007) and potassium (Echalar et al., 1995). Isotopic ratios from atmospheric CO_2 or CH_4 in ice can distinguish between fossil-fuel combustion; methane and non-methane hydrocarbons; and biomass burning (Fischer et al., 2008; Wang et al., 2010). In particular, Legrand and DeAngelis (1996) confirm the use of ammonium formate and oxalate concentrations to determine forest fire emissions recorded in Greenland ice.

Although these studies provide fundamental information to improve our understanding of past atmospheric chemistry, biomass burning is not the only source of these chemical species in the atmosphere. Soot, charcoal and black carbon may be residual products from fossil-fuel burning (Elias et al., 2001; Hansen and Nazarenko, 2004; McConnell et al., 2007). While oxalate mainly results from the evolution of organic matter in atmospheric aerosols, atmospheric oxalate arguably can also be formed through vehicle emissions (Kawamura and Kaplan, 1987). Atmospheric ammonium and ammonia can be produced by lightning and soil processes (Legrand et al., 1998; Olivier et al., 2006) or result from agricultural activity (Hristov et al., 2011). Water-soluble potassium can be transported with sea salts, while elemental potassium can arrive at glacier surfaces with mineral aerosols (Laj et al., 1997). Potassium can also be a product of biological activity (Rankin and Wolff, 2000). Due in part to higher ambient air temperatures in low-latitude ice, it is difficult to extract a climate signal from CO_2 or CH_4 in ice outside of polar regions. Therefore, a source-specific indicator is necessary to unequivocally determine past biomass burning recorded in snow and ice.

Biomass burning injects particles with adsorbed compounds into smoke plumes that can enter the global atmosphere (Simoneit, 2002). Important molecular markers for tracking the transport of biomass burning particles include monosaccharide anhydrides, such as levoglucosan (1,6-anhydro-β-D-glucopyranose), mannosan and galactosan (Simoneit, 1999). Levoglucosan is unambiguously a degradation product derived from cellulose burning at temperatures greater than 300°C (Simoneit, 2002; Schkolnik and Rudich, 2006). Monosaccharide anhydrides including levoglucosan are emitted in large quantities into the fine particle phase of smoke and are globally pervasive (Simoneit, 1999; Jordan et al., 2006; Bourcier et al., 2010). Levoglucosan returns to the surface by wet and dry deposition (Stohl et al., 2007), where it is eventually trapped and preserved in glaciers and ice sheets.

Air filter and acidic solution studies determined that levoglucosan is stable in the atmosphere for at least 10 d, even in acidic conditions (Locker, 1988; Fraser and Lakshmanan, 2000). However, recent studies outline reactions between hydroxyl radicals and levoglucosan to form higher molecular weight compounds under atmospherically relevant conditions (Holmes and Petrucci, 2006, 2007). Field studies (Saarikoski et al., 2008) compare seasonal levoglucosan flux with potassium ion (K^+) concentrations, where K^+ is assumed to be another tracer for biomass burning emissions (Robinson et al., 2006). Seasonal changes in levoglucosan to K^+ ratios suggest that typical summer hydroxyl radical levels cause degradation of levoglucosan in biomass burning plumes (Saarikoski et al., 2008). A modelling and laboratory study shows that levoglucosan can degrade in the atmosphere under polluted continental plume conditions, where the greatest amount of degradation occurs during the humid, summer, daytime conditions while the least occurs during arid, winter, nighttime conditions (Hoffmann et al., 2010). The degradation of levoglucosan under other environmental conditions is still unknown. Hoffmann et al. (2010) argue that due to this atmospheric degradation, researchers should exercise caution when attempting to estimate the amount of combusted biomass. We do not attempt to determine the mass of combusted material but are instead interested in the occurrence of fire events, and the specificity of levoglucosan helps denote past fire activity. While a percentage of levoglucosan in smoke does degrade in the atmosphere, the high concentration of levoglucosan emissions suggests that levoglucosan is a viable tracer for biomass burning (Holmes and Petrucci, 2006, 2007) and can also be used in conjunction with other chemical indicators (Koch et al., 2006).

The strength of using levoglucosan as a recorder of past fire activity lies in its specificity (Simoneit, 1999) and its availability in many continental archives (Elias et al., 2001). Here, we compare snow pit levoglucosan concentrations with other paleofire chemical indicators and with direct atmospheric measurements of fire emissions. As both levoglucosan and climate parameters are measured from

the same snow or ice strata, the multiproxy record of snow pits and by extension of ice cores presents an ideal material to investigate the links between fires and climate.

2. Experimental section

2.1. Study site and sampling procedure

The snow samples were collected in June 1995 at a remote site in the Summit area in Central Greenland (72°20′N, 38°45′W; 3270 m a.s.l., mean snow accumulation rate 23 g of water equivalent cm^{-2} yr^{-1}). The sample area was located 30 km south–west of the Eurocore/GRIP and 20 km south of the GISP2 sites in order to minimise or prevent possible contamination from the ice core drilling activities. Suttie and Wolff (1993) demonstrated that these distances are sufficient to prevent local contamination in polar sites. A remote summer camp approximately 3 km from the sample area is a possible source of contamination. In order to provide the cleanest possible environment, the camp was powered by solar panels although gas ovens were used for cooking. Snowmobiles provided transportation between the remote summer camp and the snow pit, but they were never allowed within 500 m of the pit. The predominant wind direction near Summit is from the south (Beyersdorf et al., 2007). The snowmobiles were parked on the main flag line between GISP2 and the atmospheric sampling station. All sampling materials were hand-carried 500 m to the East from the snowmobiles to the sampling site.

The 3 m snow pit was dug by hand using nitric acid-cleaned polyethylene (PE) shovels and scrapers to smooth the wall surfaces. Each person working in the snow pit, including during the initial digging, wore full clean room clothing and shoulder-length PE gloves. A continuous series of 68 samples were collected from the surface to a depth of 2.7 m. All field sampling materials were previously cleaned using strict standardised procedures (Planchon et al., 2001) with ultra pure water produced by coupling a Milli-RO with a Milli-Q system (Milipore, Bedford, MA, USA) and suprapur-grade HNO_3 (65% Merck). Previously cleaned low-density polyethylene tubes (4 cm diameter, 40 cm length) were horizontally hammered into the snow pit walls until obtaining at least 200 g of sample. Each sample was transferred from the sampling tubes to 1 L low-density polyethylene wide mouth cleaned Nalgene bottles. Each bottle was immediately sealed in two cleaned polyethylene bags and remained frozen until analysis.

All samples were transferred in a frozen state to the laboratories at the University of Venice, Italy, where they were stored at -20 °C. To the best of our knowledge, the samples did not degrade under these storage conditions. This assumption is consistent with the literature where Simoneit and Elias (2000) analyse levoglucosan on air filters that have been archived for 25 yrs without any apparent degradation. Simoneit and Elias (2000) control this lack of degradation in stored samples by reanalysing lipid compounds that were determined 25 yrs ago (Simoneit, 1977), and the recent results are similar to the original measurements. Simoneit and Elias (2000) and Simoneit (1977) studies do not explain how the samples were stored but other levoglucosan studies have stored their samples at -20 °C, in similar conditions to our work, and do not report sample degradation (Sang et al., 2011). The degradation of levoglucosan in stored ice samples should be analysed in future studies, and/or levoglucosan concentrations should be determined in snow and ice samples as soon as possible after their collection.

2.2. Sample analysis

The major ions were measured at the Laboratoire de Glaciologie et Géophysique de l' Environnement (C.N.R.S.) in the summer and autumn of 1995 using a DIONEX 100 chromatograph, with a CS12 column and a 500 mL injection loop. The trace elements were determined at the University of Venice in 2002 using a Finnegan MAT Element ICA-SFMS. The details of the major ion and trace element methods are available in Barbante et al. (2003) and references within the text.

The levoglucosan determination was conducted at the University of Venice in 2007. A total of 16 samples corresponding to the years 1994 and 1995 (from the 1995 surface to 120 cm depth) were melted in their sampling containers at room temperature under a class 100 clean bench. Samples below 120 cm depth were no longer available and therefore we were not able to determine levoglucosan concentrations for the entire snow pit. Samples were transferred to 700 μL polyethylene vials (Agilent Technologies, Wilmington, NC, USA) using Eppendorf pipettes and polyethylene tips (Hamburg, Germany). Each individual sample consisted of 675 μL of melted snow and was injected with 25 μL of an internal labelled standard of levoglucosan $^{13}C_6$ (98% isotopic enrichment, 98% purity, Cambridge Isotope Laboratories Inc., Andover, MA, USA) with a concentration of 50 pg mL^{-1}. Response factors were created using a concentration of 50 pg mL^{-1} of labelled levoglucosan $^{13}C_6$ and 50 pg mL^{-1} of a levoglucosan standard (99.7% purity from Sigma-Aldrich, Steinheim, Germany).

The procedures for the direct determination of levoglucosan at the picogram per millilitre level in less than 1 mL of polar snow or ice are described in detail in the study by Gambaro et al. (2008). Briefly, the sample analysis was performed by using liquid chromatography/negative ion electrospray ionisation – tandem mass spectrometry (HPLC/(-)ESI-MS/MS). An Agilent 1100 Series HPLC

system (Agilent, Waldbronn, Germany) with a binary pump, vacuum degasser, autosampler and thermostated column compartment was used. For the chromatographic analysis, 100 μL of the sample was injected into a C18 Synergy Hydro column (2.1 mm i.d. × 50 mm length, 4 μm particle size, Phenomenex, Torrance, CA, USA). Isocratic elution was used at 180 μL min^{-1} using a 15% v/v methanol solution in water, and a 13 mM solution of ammonium hydroxide was added on-line after the chromatographic column at a flow of 5 μL min^{-1}. An API 4000 triple quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX, Toronto, Ontario, Canada) equipped with Turbo V™ source was used to determine levoglucosan in Greenland snow. Data were collected in negative ion mode by multiple reaction monitoring with a 200 ms dwell time/transition. Sample quantification used transitions of 161/101 m/z for levoglucosan and 167/105 m/z for labelled levoglucosan.

The extremely low levoglucosan concentrations in polar snow samples necessitate precise evaluation of blanks in each step of the analytical procedure. A full description of the quality assurance of the analytical method is reported in the study by Gambaro et al. (2008). In this study, blank values were 3 pg mL^{-1}, and the detection limits were quantified as three times the standard deviation of the procedural blanks ($n = 6$), resulting in a mean value of 3 pg mL^{-1}. The blanks and detection limits were lower than the minimum levoglucosan concentrations detected in the Greenland snow samples. The repeatability was calculated as the relative standard deviation from five consecutive measurements and ranges from 20% for a levoglucosan concentration of 20 pg mL^{-1} to 50% for a concentration of 9 pg mL^{-1}. The recovery in replicate analyses of samples spiked with 17 pg mL^{-1} of labelled levoglucosan was 95% with a coefficient of variation (CV%) of less than 2%. Each Greenland snow sample was spiked with 25 μL of 50 pg mL^{-1} and was analysed three times to evaluate precision for individual samples in an environmental matrix. The CV% ranged from 2.3% for samples with concentrations near 500 pg mL^{-1} to a maximum of 38.2% for a sample with a concentration of 11.8 pg mL^{-1}. The average CV% for all samples is 13.5%. In order to better control if samples degradated under the storage conditions in the −20 °C freezer, the levoglucosan samples were reanalysed in the fall of 2011 and resulted in concentrations at, or slightly above, the concentrations measured in 2008.

3. Results and discussion

3.1. Correspondence between atmospheric and snow samples

The US Greenland Ice Sheet Project 2 atmospheric component (ATM) and the European Community Transfer of Aerosols and Gasses to Greenland Snow and Ice (EC-TAGGSI) specifically investigated air masses with biomass burning signatures. During the Summit, Greenland field seasons of 1992–1995, Jaffrezo et al. (1998) recorded daily aerosol carboxylic acid [including formate, $HCOO^-$ and oxalate, $(C_2H_2O_4)^{2-}$] concentrations. On 5 August 1994, oxalate concentrations in the aerosol at Summit (~3.0 nM m^{-3}) were two orders of magnitude greater than the background level (~0.02 nM m^{-3}) (Dibb and Jaffrezo, 1997). The air masses with high oxalate concentrations also contained increased atmospheric NH_4^+ and K^+ concentrations, further suggesting the influence of biomass burning emissions (Dibb et al., 1996; Jaffrezo et al., 1998).

Regional severe forest fires burned in Alberta and Saskatchewan between 29 July and 3 August 1994 (Miller and O'Neill, 1997). This episode is detailed in the literature through observations of forest fire smoke aerosols at multiple atmospheric altitudes in northern and central Canada when the smoke aerosols passed over the Boreal Ecosystem-Atmosphere Study between 28 July and 31 July 1994 (Miller and O'Neill, 1997). The timing of the forest fires and smoke transport over Canada is consistent with the atmospheric aerosol measurements at the Summit, Greenland study site (Dibb and Jaffrezo, 1997). HYSPLIT isotropic back-trajectory analyses (Fig. 1) demonstrate that air masses from these known Canadian forest fires reached the Summit, Greenland study site and are the likely source of the measured elevated carboxylic acid concentrations (Draxler and Rolph, 2011; Rolph, 2011). We used isentropic trajectories as they incorporate vertical transport components and best integrate the vertical difference between the HYSPLIT model and the NCAR reanalysis data. The transport time from the Western Hudson Bay, Canada source region to Greenland is 3–4 d (Dibb et al., 1996; Jaffrezo et al., 1998), which is within the atmospheric lifetime of biomass burning aerosols such as levoglucosan (Fraser and Lakshmanan, 2000; Simoneit, 2002). In addition to identifying the source of the smoke aerosols during the forest fire events, our results are consistent with 44-yr back-trajectory averages to Summit, demonstrating that the majority of summer trajectories originate over North America (Kahl et al., 1997).

Snow falling when the biomass burning plumes were above the study site and surficial 5 August 1994 snow samples include large enrichments in CH_3COO^-, $HCOO^-$, NH_4^+ and K^+ concentrations, supplying evidence for the transfer of biomass burning aerosols to the ice cap surface. The snow samples do not record an exact representation of the composition of the smoke plume, but do bear an unambiguous fire signature (Dibb et al., 1996; Jaffrezo et al., 1998). The Summit surface snow NH_4^+ and $HCOO^-$ peaks (Dibb et al., 1996) have similar concentrations as Greenland ice core NH_4^+ and $HCOO^-$ peaks that are

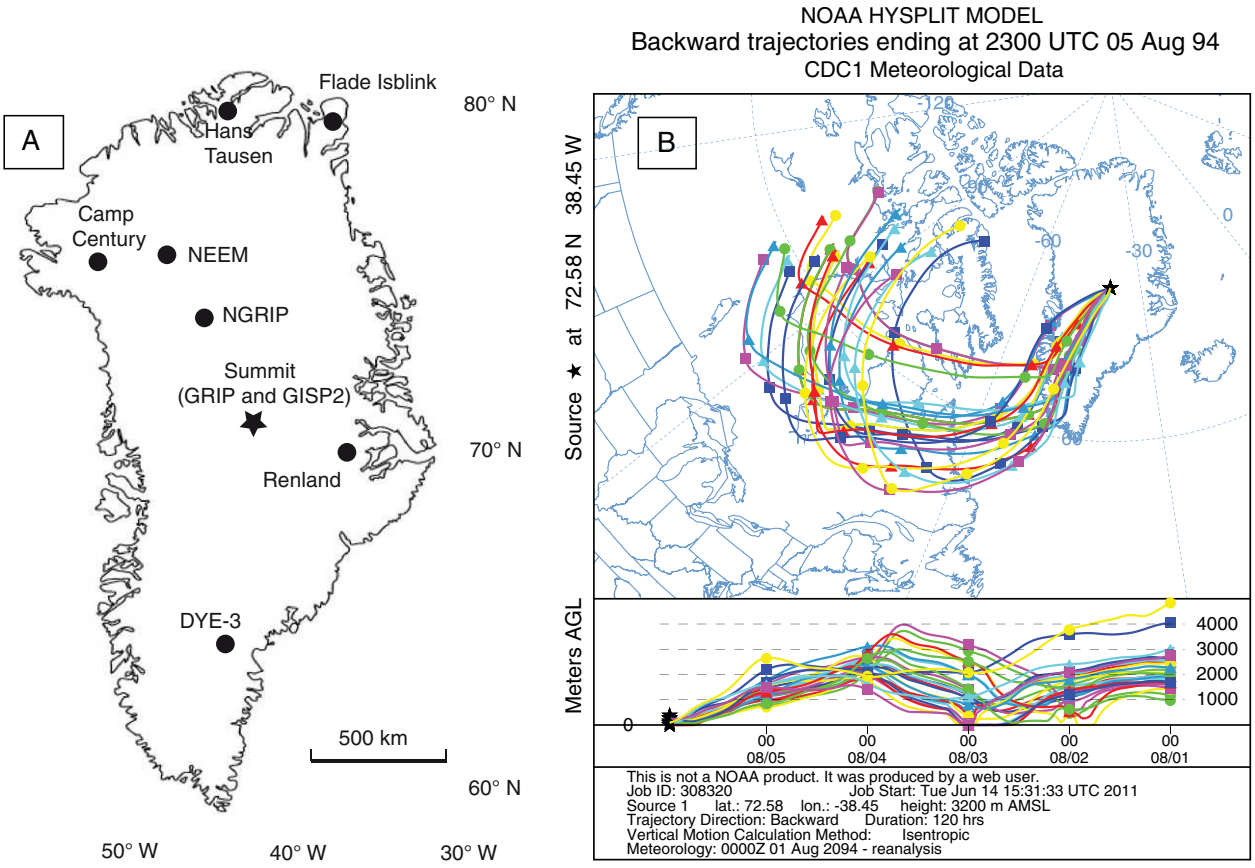

Fig. 1. (A) Site location (star) in relation to major Greenland ice core drilling sites (filled circles). (B) Isentropic back trajectories for air masses arriving to Summit, Greenland on 5 August 1994 calculated using NCAR reanalysis data and the HYSPLIT model.

recognised biomass burning events (Legrand et al., 1992), suggesting that modern events are similar to those present in the paleorecord. This combination of data links smoke plumes, associated aerosols, snow deposition and compaction into glacial ice.

3.2. *Levoglucosan and oxalate concentrations in Greenland snow samples*

Using these links between sources, atmospheric transport and deposition, we determined levoglucosan concentrations in snow pit samples that encompass the years surrounding the August 1994 biomass burning event at a depth of approximately 50 cm (Fig. 2). Increased cyclogenesis in the North Atlantic deposits greater concentrations of sea salts on the Greenland Ice Sheet during the boreal winter, resulting in Na^+ peaks (Barbante et al., 2003). Seasonality demonstrated in Na^+ peaks (spring) is validated by less negative oxygen isotope ratios (summer) in the same snow pit samples (Gabrielli et al., 2008). Biomass burning markers including oxalate, NH_4^+ and K^+ were previously reported in the study by Barbante et al. (2003), and levoglucosan was determined from aliquots of the same snow samples. Levoglucosan concentrations in Summit, Greenland snow samples from 1994 to 1995 range from 11 to 597 pg mL^{-1}, while oxalate concentrations measured from the same snow pit and across the same time span range between 0.1 and 9.5 ng mL^{-1} (Fig. 2). Levoglucosan concentrations replicate the August 1994 oxalate concentrations, demonstrating its use a proxy for past biomass burning in snow pit samples. Levoglucosan is a more specific marker of past fire activity than is oxalate, as it can only be produced by cellulose burning at temperatures above 300°C.

The oxalate and levoglucosan concentration peaks occur during the summer of 1994, coinciding with the known Canadian forest fire event (Dibb et al., 1996). The maximum levoglucosan concentrations and relative background levels replicate the previously measured oxalate concentrations (Fig. 2b), suggesting a common origin in the fallout of these two biomass burning indicators in Greenland snow. Other than oxalate, NH_4^+ is the only other biomass burning indicator with moderately increased concentrations during the known deposition of forest fire aerosols in the summer of 1994 (Fig. 2). The NH_4^+ peak is

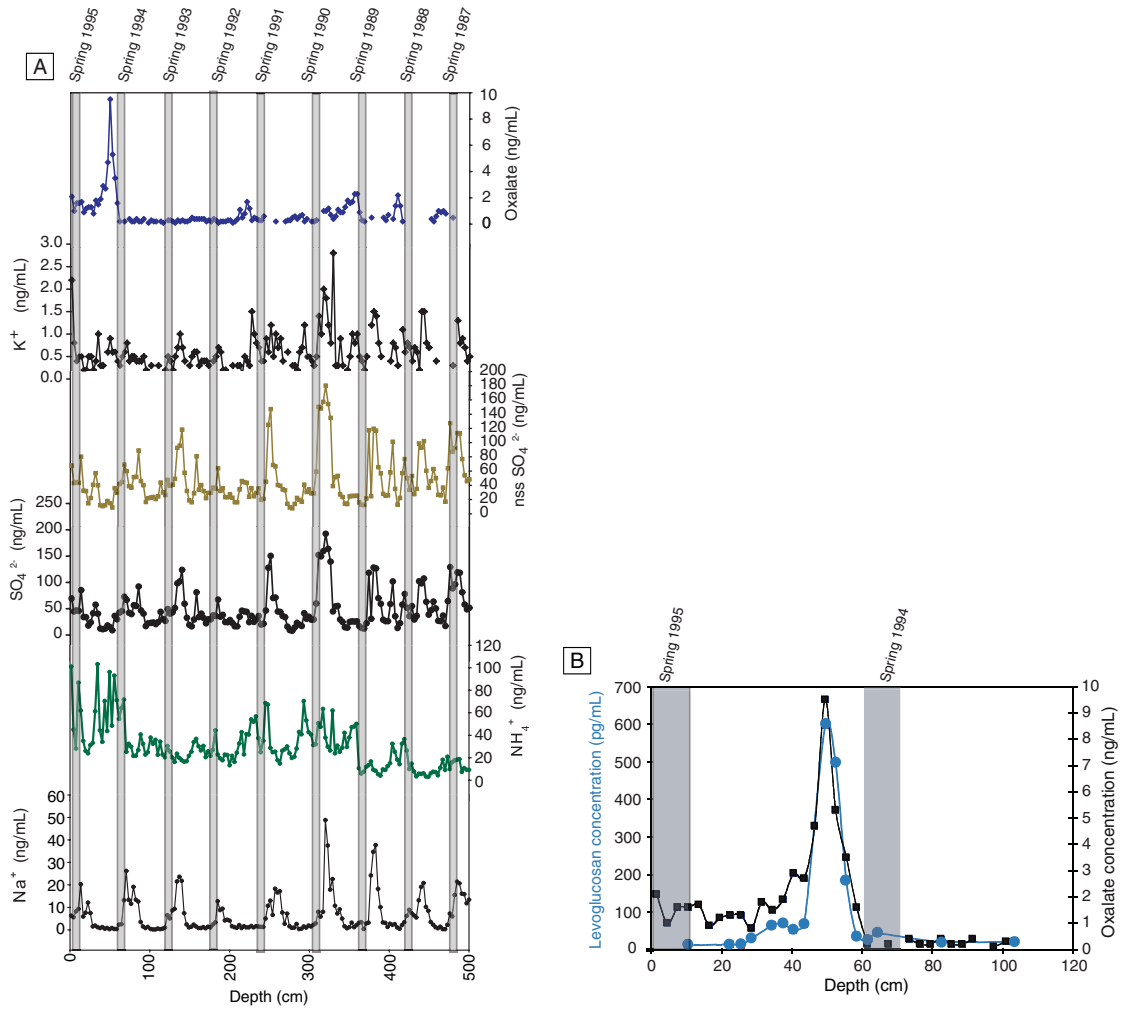

Fig. 2. (a) Biomass burning indicators recorded in a Summit, Greenland snow pit. Sodium (Na^+) peaks determine the seasonality and annual layers where spring (March, April and May) deposition is assumed to occur above each Na^+ peak. Oxalate, SO_4^{2-} and Na^+ data were previously published in Barbante et al. (2003). (b) Detail of levoglucosan (light blue circles) and oxalate (dark blue squares) concentrations in the upper meter of the snow pit.

more diffuse than the oxalate signal, and the NH_4^+ concentrations remain high throughout the summer rather than outlining a well-defined single event. Other markers that are used in the literature to indicate biomass burning in ice cores and snow pits (K^+ and nss SO_4^{2-}) do not peak in parallel with the oxalate and levoglucosan.

Varying post-depositional atmosphere and snow interactions may account for part of the differences between biomass burning proxies. Oxalate is incorporated in or on ice crystals (Dibb and Jaffrezo, 1997). NH_4^+, K^+ and nss SO_4^{2-} tend to be associated with particles when they are deposited through dry deposition (Bergin et al., 1994). Aerosol particles can be reintrained and be blown away from the glacier surface, while carboxylic acids such as oxalate may be sensitive to post-depositional processes (Dibb and Jaffrezo, 1997).

Little is known regarding levoglucosan and oxalate deposition and transfer to the snow surface. However, the literature contains studies examining the atmospheric transport of levoglucosan, oxalate and other organic biomarkers as well as post-depositional processes affecting the species once they are in the snowpack. Saccharides including levoglucosan have low atmospheric vapour pressures and are transported in the particulate phase (Oja and Suuberg, 1999) before being deposited by wet and dry deposition (Stohl et al., 2007). Reid et al. (1998) examined gas to particle formation in smoke plumes and determined that NH_4^+ and oxalate are highly correlated, suggesting that the formation processes are similar. NH_4^+ and SO_4^{2-} did not correlate, suggesting that SO_4^{2-} is not related to organic acid formation. This atmospheric correlation between NH_4^+ and oxalate does not extend to the studied snow pit, where the

concentrations of the two species differ (Fig. 2a). This lack of correlation between NH_4^+ and oxalate in the snow pit suggests that post-depositional processes affect one or both species. Levoglucosan is known to degrade in the atmosphere with exposure to hydroxyl radicals (Holmes and Petrucci, 2006, 2007), and increased levels of hydroxyl radicals have been measured in the air above the snowpack at Summit, Greenland during periods of high winds (Sjostedt et al., 2007). Past research of organic carbon in a snow pit similar to that used in this study and located near Summit, Greenland suggests that post-depositional process including photochemical reactions during sunlit periods caused significant depletion of organic carbon within the snowpack (Hagler et al., 2007). The authors determine that although post-depositional processes do occur in aged snow, the fact that the organic compounds still exist suggest that they may still be useful for linking past atmospheric concentrations with ice core records.

As the transport and depositional history of smoke plumes resulting in the oxalate and levoglucosan peaks are well known (Dibb et al., 1996; Jaffrezo et al., 1998), the absence of peaks in other traditionally used biomass burning markers reinforces the fact that the multiple sources of these markers may sometimes have a greater impact than the contribution of biomass burning to their signal. As levoglucosan is unambiguously derived from past cellulose fires, it is a specific marker of biomass burning. This specificity is further demonstrated by the fact that levoglucosan concentrations are close to background levels on either side of the fire emissions peak, whereas oxalate concentrations remain relatively elevated and variable after the forest fire peak (Fig. 2b). When used in conjunction with NH_4^+, K^+ and nss SO_4^{2-}, levoglucosan may also be used to determine the relative contribution of biomass burning versus the contribution of other sources.

4. Conclusions

Ice core records and snow pit samples have previously lacked a specific marker for past biomass burning. Indicators such as oxalate, ammonia and potassium ions that have been used as proxies for past fire events in ice cores have more than one source. Isotopic ratios and mixing ratio measurements of CO_2 and CH_4 in ice can distinguish between methane, fossil-fuel and biomass burning sources (Fischer et al., 2008; Wang et al., 2010), but the difficulty of analysing CO_2 and CH_4 in low-latitude ice cores makes these techniques primarily applicable to polar areas. Here, we demonstrate the applicability of direct determination of levoglucosan concentrations in snow pit samples as a specific marker for past fire activity. The levoglucosan concentrations in Summit, Greenland snow samples replicate the oxalate peak recorded in the same samples, demonstrating the reproducibility between the two proxies, although levoglucosan is a specific marker of biomass burning while oxalate incorporates other sources. Peaks in both levoglucosan and oxalate concentrations correlate with direct atmospheric measurements of a known biomass burning event whose advected fire emissions reached the study site. Levoglucosan is thus measurable in snow samples where the depositional history suggests that it should be present, and does not appear to be destroyed in the early firnification process. Future work should investigate seasonal to decadal conservation of levoglucosan in snow samples subjected to melting and refreezing cycles and/or conversion to glacier ice.

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